

# The concepts of work and heat and the first and second laws of thermodynamics

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## Abstract

A simple and effective approach to thermodynamics is suggested, which solves the major difficulties in the traditional presentation of the subject. The internal energy is introduced from the behavior of deformable bodies, whereas the importance of keeping in mind the microscopic picture is emphasized. A straightforward model is used to show that the internal energy depends on the volume and entropy, from where the relationship between mechanics and thermodynamics is immediate, mechanics corresponding to isentropic thermodynamics. The questions of evolution to equilibrium and irreversibility are studied under the light of the action of the “dynamic force,” which has a dissipative character. The present formulation leads to a discussion and clarification of the physical meaning of various thermodynamic quantities, such as pressure, temperature, work and heat. The adiabatic piston problem is analyzed, as a paradigmatic case where the notions of “adiabatic” and “heat transfer” are often ill-defined.

## I. INTRODUCTION

Thermodynamics has been, still is and will remain to be one of the key disciplines of physics and chemistry. However, in its traditional form it has recurrently brought intellectual resistance. For instance, there is a famous story about Arnold Sommerfeld and thermodynamics that is cited in several sources<sup>1,2</sup> and spreads on the internet. When Sommerfeld was asked why he had never written a book on thermodynamics, since he had written books on nearly every topic of physics, his humorous answer was “Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don’t understand it, but by that time you are so used to that subject, it doesn’t bother you anymore.” Actually Sommerfeld died in 1951 and at the time he was writing a book on thermodynamics and statistical mechanics, which was published after his death.<sup>3</sup> The interesting fact in this story is that thermodynamics, despite being well established for many years and dealing with apparently simple and intuitive concepts, nevertheless remains quite difficult and subtle.

We believe the difficulties with thermodynamics arise essentially from two main factors. The first one is the traditional development of the concepts and the formalism using the variable *temperature*. As it is well-known, the natural variables associated with the internal energy  $U$  are the *volume* and the *entropy*, which allow to Legendre transform  $U$  into the other thermodynamic potentials and flank it on the “thermodynamic square.”<sup>4</sup> Temperature and pressure can then be readily obtained from Maxwell’s relations. We consider that a formulation of thermodynamics made considering from the beginning  $U = U(S, V)$  contributes to a neat mathematical derivation and an easier understanding of the meaning of the different symbols. An early introduction of the entropy was also proposed by Herbert Callen.<sup>5</sup>

A second difficulty comes from the fact that thermodynamic quantities such as temperature and pressure are defined in equilibrium. The application of the formalism to non-equilibrium processes makes several variables and notions lose their intuitive physical meaning and the mere use of the words denoting these variables may induce in error. The difference between the static and dynamic pressures is crucial and is thoroughly discussed in this paper. Another paradigmatic example is the “adiabatic piston” problem briefly

reviewed in Section IV C, where the word “adiabatic” is itself problematic.

Richard Feynman, in the very first chapter of his “Lectures on Physics,”<sup>6</sup> addresses his students in the following way: “If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed to the next generations of creatures, what sentence would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the *atomic fact*, or whatever you wish to call it) that *all things are made of atoms – little particles moving around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*” We like to recall this remarkable start of Feynman’s “Lectures.” Its pertinence to the present paper resides in the fact that one way to minimize the difficulties surrounding thermodynamics is to always keep in mind the microscopic mechanisms in which it is founded.

In this paper we want to suggest a way to avoid most of the traps frequently encountered in the presentation of thermodynamics. To this purpose, we put forward a development where we try to keep the ideas very simple, by maintaining a natural and strong connection with mechanics and the microscopic view. We start by making the link between mechanical energy and the internal energy of deformable bodies in Section II. In Section III we use a simple and clear “base model” to show that the internal energy cannot be a function only of the deformation variable. Entropy is introduced and the relationship with mechanics is immediate: mechanics is isentropic thermodynamics. The second law and the questions of evolution to equilibrium and irreversibility are also addressed in Section III, which finishes with the presentation of the formalism. Heat and the first law of thermodynamics are introduced in Section IV, from generalizations to the base model. The important case of the adiabatic piston is analyzed in this chapter as well, as an illustration of the advantages of the proposed approach. Further extensions of the model, leading to the detection and clarification of additional nuances, are pointed out and briefly debated. The main findings are reviewed and discussed in Section V, which concludes the paper.

## II. WORK AND ENERGY: MECHANICS AND THERMODYNAMICS

As it is well-known, the concepts of *work* and *energy* were developed empirically, associated first with the notions of *force*, *gravitational potential energy* and *kinetic energy*. The complexity of the action of muscles was substituted by a simplified description of a static

force, which can be measured, for instance, by a dynamometer. This lead to the notions of *weight* as a force, as well as of the corresponding opposing force present in equilibrium. The concepts of work of the weight and work of the force opposing weight appear naturally from here. The idea of gravitational potential energy arises from the design and construction of weight lifting machines.

All these intuitive concepts are very fundamental and part of any introductory study of physics. Among many excellent textbooks available, we would like to recall the brilliant presentation of the subject by Feynman,<sup>6</sup> who introduces it following the route just described. Another hypothesis, which he immediately advances and was early noted by Leonardo da Vinci,<sup>7</sup> is that “there is no such thing as perpetual motion with weight lifting machines.” Feynman moves on to warn that “in fact, that there is no perpetual motion at all is a general statement of the law of conservation of energy.”

Newton’s laws allow a general description of motion. The identification of the variation of the kinetic energy as the work done by the resultant or net force applied to a particle of a certain mass is one of the results of the theory. Putting together gravitational potential energy and kinetic energy we have the conservation of mechanical energy, valid for a system moving only under the effect of the gravitational force.

The generalization of these ideas to extended deformable bodies is at the origin of the notion of *internal energy*. A very simple example is depicted in Figure 1a). A pair of forces of the same magnitude and opposite directions acts on a body, deforming it. Clearly, there is work done by the forces, but the translation kinetic energy and the gravitational potential energy of the body remain unchanged. This straightforward example illustrates as well the power of the microscopic view as a model for thought. The most simple microscopic picture is to imagine the body as an ideal gas in a container with movable walls, Figure 1b). In this case the work done is converted in kinetic energy of the constituents of the gas, which is in fact its internal energy.

With further maturation, this extension of the concepts of mechanics to deformable bodies is at the genesis of thermodynamics. Historically, however, thermodynamics evolved in a rather autonomous way. Its development was based on the concepts of heat and temperature, with properties apparently foreign to the phenomenology described by mechanics. These two new concepts were not easily encompassed by the formalism of mechanics, although there have always been “kinetic” conceptualizations of the thermodynamic quantities.<sup>8</sup>

The application of Newtonian physics to engineering, military engineering being of particular importance, forced mechanics to face the question of *friction*, which is always present in practice. Friction was – and still is – treated as a phenomenon which is not an essential part of mechanics. One recurrent statement revealing the attempt to isolate mechanics from the phenomenology of friction is the affirmation of the reversibility of the equations of mechanics.

Friction brings to light that mechanics and thermodynamics are one and the same subject. The works of Maxwell and Boltzmann culminate an amazing effort of many authors to conciliate mechanics with thermodynamics, addressing the question of evolution to equilibrium. Boltzmann, in particular, proposing a microscopic interpretation of entropy,<sup>9,10</sup> opens the door for a reevaluation of the meaning of several concepts, still problematic in the basic formulation of thermodynamics nowadays.<sup>11,12</sup> Let us pass through the door and travel this road in the remaining of this paper.

### III. ENERGY AND ENTROPY: THE BASE MODEL

Thermodynamics is established for a long time and there is a relatively consensual view on the way to present it. Most concepts, such as work, temperature and heat, are usually introduced from the very beginning and in a very intuitive way. Despite these facts, various difficulties arise in the interpretation of some fundamental quantities – heat and work on the first line – even in quite simple situations. The subtleness of these seemingly simple and unambiguous notions, lead to a permanent search for consistency in the definitions of work and heat in the formulation of the first and second laws of thermodynamics, still very active nowadays.<sup>13–23</sup>

We suggest an early introduction of the variable entropy, postponing the appearance of the quantities temperature and heat. This approach allows a formulation of thermodynamics that uses from the beginning the natural variables associated with the internal energy, which are the volume and the entropy. Moreover, all remaining quantities are introduced in a very general and clear way, which, we believe, helps preventing the misunderstanding and errors that spread even in the scientific literature. Finally, this procedure immediately provides an easily identifiable connection between mechanics and thermodynamics.

### A. The need for the variable entropy

Thermodynamics can be introduced with generality from a clear, uncomplicated, “base model,” corresponding to one of the most typical systems in thermodynamics: a classical ideal gas in a container with a movable piston on top, under the action of gravity, as shown in Figure 2. The system is surrounded by vacuum, so that there is no external atmospheric pressure on the piston. There is no friction between the piston and the container walls. Furthermore, it is assumed that the piston and the container walls do not have any internal structure, so that all collisions between the gas particles and the piston or the containing walls are perfectly elastic. This system can be studied starting only with the notions of weight, work done by the weight, gravitational potential energy and internal energy. Note that a similar system was used by Kivelson and Oppenheim to discuss the concept of work in irreversible processes.<sup>24</sup>

Let us assume that the gas initially occupies a volume  $V_1$  and exerts a pressure  $P_1$  on the container walls. The piston is held fixed in its place. Its total mass,  $M$ , is such that the pressure exerted by the piston as soon as it is released,

$$P_e = \frac{Mg}{A} , \quad (1)$$

is larger than  $P_1$ ,  $A$  denoting the area of the base of the piston.

The final equilibrium position of the piston can be determined if we know the dependence of the gas pressure with the gas internal energy. For a classical monoatomic ideal gas, from the microscopic picture and the calculation of the average momentum transfer per unit time it is easy to show that this relation is

$$P = \frac{2}{3} \frac{U}{V} = \alpha \frac{U}{V} \quad (2)$$

(notice that in fact all results can be obtained assuming the relation  $P = \alpha(U/V)$ , where  $\alpha$  is a constant parameter dependent on the gas, which describes also the cases of diatomic and polyatomic ideal gases, as well as the relativistic gas of photons with  $\alpha = 1/3$ ) As a matter of fact, for a container of dimensions  $L \times L \times L$ , a particle of mass  $m$  and speed  $v_x$  moving along the  $x$  direction hits one of the walls  $v_x/2L$  times per unit time, and in each collision transfers a momentum  $2mv_x$ . Thus, the momentum transfer per unit time to the wall is  $mv_x^2/L$ . If we have  $N$  particles moving along the  $x$  direction and with different

speeds, the average momentum transfer per unit time is  $\langle \Delta p / \Delta t \rangle = Nm \langle v_x^2 \rangle / L$ , where  $\langle v_x^2 \rangle$  is the average value of  $v_x^2$ . Further assuming that there is no privileged direction of motion,  $\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = 3 \langle v_x^2 \rangle$ . Finally, dividing by the area  $L^2$  to obtain the pressure,

$$P = \frac{1}{L^2} \left\langle \frac{\Delta p}{\Delta t} \right\rangle = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle, \quad (3)$$

which is Equation (2) identifying the internal energy with the kinetic energy of the gas. Take note that the potential energy of the constituents of the gas is negligible in regard to their kinetic energy. Furthermore, all the main results derived below do not depend on this approximation.

It is worth noting that, *despite the absence of friction, the piston does reach a final equilibrium position* and does not remain oscillating indefinitely. Or, more precisely, will at first oscillate while slowly evolving to its equilibrium position and, once this position is reached, the piston stays *jiggling* around it. What happens is that the pressure exerted by the gas on the piston is a “dynamic pressure”.<sup>20–23</sup> For the same volume, the dynamic pressure is higher in a compression and lower in an expansion.<sup>20–22</sup> The piston moves under the action of the weight and of the dynamic force. Because of the unbalance between both forces, the latter has a “dissipative character,” leading the piston to the final equilibrium position.<sup>21</sup> The situation is somewhat similar to the case of a bullet entering at high speed in a region where there is a gas at room temperature. Even if all collisions between the gas particles and the bullet are perfectly elastic, the net effect is one of slowing down the bullet, until it finally stops. We will return to this point in Section V, where a one-dimensional version of our base model, interesting as a model of thought and adequate for numeric simulations, is also suggested.

The final equilibrium position can be calculated from the principle of conservation of energy and the equality of the gas and piston pressures. The former corresponds to state that the decrease in the gravitational potential energy must correspond to an increase in the internal energy,

$$-Mg(h_2 - h_1) = U_2 - U_1, \quad (4)$$

where the indexes 1 and 2 refer to the initial and final states, respectively, and  $h$  is the height of the piston,  $h = V/A$ ; the latter is the statement

$$\frac{Mg}{A} = \alpha \frac{U_2}{V_2}, \quad (5)$$

where Equation (2) was used. We have as well

$$U_1 = \frac{P_1 V_1}{\alpha} , \quad (6)$$

so that

$$h_2 = h_1 \frac{\alpha}{1 + \alpha} \left( 1 + \frac{P_1 A}{Mg\alpha} \right) . \quad (7)$$

If  $P_1 < P_e$ , as we have assumed,  $h_2 < h_1$ , as it should be. Nevertheless, Equation (7) is valid for any relation between the initial gas pressure  $P_1$  and  $P_e$ .

Let us now assume we remove a certain mass from the piston (for instance, we can imagine that the piston has several masses on the top of it, and we can thus remove to the side one of them). The new total mass of the piston is  $M' < M$  and the piston will reach a new equilibrium position, which we identify with the subscript 3. Let us look at the case where  $M'$  is such that the new equilibrium position,  $h_3$ , is the same as the initial position  $h_1$ . The energy conservation between positions 2 and 3 reads, similarly to Equation (4),

$$- M'g (h_1 - h_2) = U_3 - U_2 . \quad (8)$$

Therefore, combining this expression with (4), we arrive at the following very interesting result

$$U_3 - U_1 = (M - M')g (h_1 - h_2) > 0 . \quad (9)$$

Thereby, when the piston goes back to its initial volume, the internal energy of the gas is higher than the initial one. It is straightforward to show that this conclusion remains valid if initially we would have  $P_1 > P_e$  and hence  $h_2 > h_1$  and  $M' > M$ .

Equation (9) means that the internal energy cannot be solely a function of the volume, in contrast to the typical situations of mechanics (where the potential energy is only a function of position). If we assume that one further variable suffices to completely determine the internal energy, then we can write

$$U = U(V, S) . \quad (10)$$

The new variable,  $S$ , is called *entropy*.

## B. Properties of entropy and the second law

Suppose now that the piston has initially a mass  $M_0$  such that  $AP_1/g = M_0$ , which means that if the piston is released it stays at its equilibrium position. We can now add to the



piston a mass  $m = (M - M_0)/2$  and wait for the piston to reach its equilibrium position. Finally, we add yet another mass  $m$  to the piston, so that its total mass is  $M$ , as in the compression described in Section III A. Using the same reasoning as above, it is not difficult to show that the final equilibrium position corresponds to a position  $h'_2 < h_2$ . This, again, shows that the internal energy cannot be uniquely a function of the volume. Moreover, the lower height reached by the piston reflects the smaller unbalance between the dynamic force exerted by the gas and the weight than in the previous case.

We can further imagine a transformation where the mass of the piston is increased in  $N$  equal steps from  $M_0$  to  $M$ , for instance by slowly adding sand grains, one by one, on the top of the piston. At each step the dynamic force exerted by the gas is nearly the same as the weight. Therefore, the dissipative character of the dynamic force practically does not manifest itself. The piston reaches the lowest possible final position corresponding to a total mass  $M$ . Figure 3 illustrates this effect, by showing the final height of the piston as a function of the number  $N$  of masses  $m = (M - M_0)/N$  added on the top of the piston. The calculations were carried out for  $M_0 = 10$  kg,  $M = 11$  kg and  $\alpha = 2/3$ . The final height is depicted as a fraction of the initial height. The reader is invited to verify that the final result is given by  $h_2/h_1 = \prod_{k=1}^N \left[ \frac{\alpha}{1+\alpha} + \frac{1}{1+\alpha} \frac{M_0+(k-1)m}{M_0+km} \right]$  and that the limiting result is  $(M_0/M)^{1/(1+\alpha)}$ . For the case depicted in Figure 3 we have  $(10/11)^{3/5} \simeq 0.944418$ .

Interestingly enough, if the sand grains are now slowly removed, one by one, we have again almost an equilibrium between the dynamic force and the weight at all times. Everything nearly returns to the initial configuration and the gas will thus have very approximately the same internal energy as in the beginning. Figure 4 shows the final height  $h'_3$  as a function of masses used both during the compression and the expansion, normalised to the initial height  $h_1$ .

Lastly, note that if we make the compression with a large number of steps, but the expansion quickly in few steps, we still find the need to add some additional mass to the piston to bring it to height  $h_1$  and  $U_3 > U_1$ , as in Equation (9). The same happens if we do the expansion slowly with a large number of steps, but the compression with few steps.

Some properties of entropy can now be easily derived. Referring to this simple case treated with the base model, we have

$$U(V, S_3) \geq U(V, S_1) . \quad (11)$$

If we arbitrate that  $S_3 \geq S_1$ , then *the entropy can only increase or remain constant*. Moreover,

$$\left(\frac{\partial U}{\partial S}\right)_V > 0 . \quad (12)$$

Clearly, the situation with no entropy change corresponds to a *reversible* transformation, *i.e.*, to a transformation where the initial state of the system can be recovered. In this case the internal energy can be calculated only from the volume, as in the typical cases of mechanics. Thereby, mechanics corresponds to *isentropic* thermodynamics, that is, to a set of transformations where the entropy does not change.

It is worth underlining two issues evidenced by the previous discussion and Figures 3 and 4. The first one is that for deformable bodies (bodies with internal structure), the isentropic transformations can only be performed by *always* keeping the system nearly in equilibrium, when the dynamic force is always approximately balanced by the “static” weight force. Failing to do so, *either in the compression or the expansion*, or both, leads to an increase of the entropy and to the impossibility of recovering the initial state of the system. The latter statement exposes the second matter: it is not necessary to look at the complete sequence compression+expansion to speak about a reversible transformation, as its reversible character, corresponding to constant entropy during the process, can be ascribed separately to the compression and to the expansion. In short, if a transformation leads from one state to a different one with the same entropy, then the transformation can be reversed, and vice-versa. The process just described of slowly adding or subtracting sand grains approaches such reversible processes.

We have thus obtained the second law of thermodynamics, while keeping its interpretation and understanding at a very fundamental level. Evidently, in many situations studied in mechanics a variation of entropy does take place, although usually it is not taken into account. An example would be the treatment of the compression depicted in Figure 1a) considering the energy only as a function of the deformation. A similar case is the deformation of a spring and the application of Hooke’s law. We will further discuss this point in Section V.

### C. Introduction of the formalism

As shown in the previous Sections, the internal energy depends (at least) on two variables, volume and entropy, as given by Equation (10). Therefore, we can write

$$dU = \left( \frac{\partial U}{\partial V} \right)_S dV + \left( \frac{\partial U}{\partial S} \right)_V dS . \quad (13)$$

The idea of the increase in entropy as a result of the lack of balance between the dynamic and the static force, advanced and discussed in the previous sections, can be confirmed as follows. The work of the resultant of the forces on the piston is equal to the variation of its kinetic energy. In differential form,

$$dE_k = -\frac{Mg}{A}dV + \tilde{P}dV , \quad (14)$$

where  $\tilde{P}$  is the dynamic pressure exerted by the gas on the piston and  $dE_k$  is the variation of the kinetic energy of the piston. On the other hand, the variation of the potential energy of the piston is

$$dE_{pot} = \frac{Mg}{A}dV . \quad (15)$$

Consequently,

$$dE_k + dE_{pot} = \tilde{P}dV . \quad (16)$$

In addition, the conservation of energy reads

$$dE_k + dE_{pot} + dU = 0 . \quad (17)$$

As a result,

$$dU = -\tilde{P}dV , \quad (18)$$

so that *the variation of the internal energy of the gas is equal to the work done by the dynamic pressure.*<sup>21-23</sup>

Among the conclusions from Section IIIB we have seen that a reversible transformation corresponds to a constant value of the entropy, so that  $dS = 0$ . What is more, the dynamic pressure is the same as the static pressure in this case. Hence, as  $dU = -P_e dV$  and  $P = P_e$ , with  $P_e$  given by (1), from (13) we have

$$dU = -P_e dV = -P dV = \left( \frac{\partial U}{\partial V} \right)_S dV . \quad (19)$$

Thus, the quantity  $P$  can be defined from

$$P = - \left( \frac{\partial U}{\partial V} \right)_S , \quad (20)$$

which corresponds to the gas pressure for an equilibrium point.

Similarly, we can define the quantity  $T$  from

$$T = \left( \frac{\partial U}{\partial S} \right)_V > 0 , \quad (21)$$

where the inequality is simply Equation (12). It is not difficult to later identify  $T$  with the ideal gas temperature. This determination has been made by other authors.<sup>5,25</sup> Notice, however, that, for an irreversible transformation,  $P$  and  $T$  are *defined* by Equations (20) and (21), respectively. In a dynamic situation, when the gas has a certain volume and a certain internal energy,  $P$  and  $T$  are the pressure and temperature *it would have if it were in equilibrium and would have the same volume and internal energy*. This is the general meaning of  $P$  and  $T$ , and no other. Furthermore, in a dynamic situation  $P$  is *not* the pressure exerted by the gas. Naming  $P$  and  $T$  “pressure” and “temperature” and thinking in physical terms in these quantities, with these designations, as defined in equilibrium, is a common source of mistakes and misunderstandings.

Finally, we can write

$$dU = -\tilde{P}dV = -PdV + TdS \quad (22)$$

and

$$-(\tilde{P} - P)dV = TdS . \quad (23)$$

This last equation establishes that *the variation of entropy is a consequence of the difference between the dynamic and the static pressures*. This difference results in the “dissipative character” of the force, *even if there is no friction*, as pointed out and discussed in section III A. This expression allows an additional verification that  $S$  always increases. As a matter of fact, if  $dV > 0$  it must be true that  $\tilde{P} < P$ , so that  $dS > 0$ . The same conclusion is obtained if  $dV < 0$ , as then  $\tilde{P} > P$ .

To finish this section, let us go back to Equation (18), to note that

$$\Delta U = - \int \tilde{P}dV , \quad (24)$$

which, denoting by  $W$  the work done by the dynamic force,

$$W = - \int \tilde{P}dV , \quad (25)$$

takes the expected form

$$\Delta U = W . \quad (26)$$

Moreover, it is immediate to verify that between two points where the piston is at rest the work done by the dynamic force  $W$  is equal to the work of the weight. Indeed, substituting (15) in (17), integrating and noting that in this case  $\Delta E_k = 0$ ,

$$\Delta U = - \int \frac{Mg}{A} dV = - \int P_e dV = - \frac{Mg}{A} \Delta V = - \Delta E_p = W . \quad (27)$$

This consistency check does not constitute a surprise, as all our analysis of the base model started precisely from this condition. The interesting fact is that, despite  $P_e \neq \tilde{P}$  along the transformation, between two points where the piston is at rest we nevertheless have

$$\int P_e dV = \int \tilde{P} dV . \quad (28)$$

If the transformation is reversible,  $dS = 0$  along the transformation and, if the gas returns to the initial volume, using Equation (22),

$$\Delta U = - \oint \tilde{P} dV = - \oint P dV = 0 . \quad (29)$$

In general, for an irreversible transformation returning to the same volume,

$$\Delta U = - \oint \tilde{P} dV > 0 . \quad (30)$$

Thus, the work of the dynamic force is transformed in internal energy, making it increase if the system returns to the initial volume, in accordance with the conclusions presented in Section III A.

In a generalisation of the concept of heat,<sup>8</sup> we can say that the work has been transformed into *heat*. Heat, however, is a subtle concept, still often misinterpreted (*cf.* Section IV C) and it would be better to rather say that “work has been used to heat the gas.” Nonetheless, with the intuition acquired on the notion of variation of entropy associated with the base model, linking Newton’s second law with the second law of thermodynamics,<sup>21</sup> we are now ready to infer the properties of more complex systems.

#### IV. HEAT: GENERALIZATIONS OF THE BASE MODEL

The natural generalization to a more elaborated configuration is the study of a system comprised of two subsystems with a common boundary, from which they can exchange

energy. We will consider various configurations. The first one corresponds to one subsystem of fixed volume with the second subsystem with a movable piston on top, leading to the formulation of the first law and the study of the heat reservoir. The second arrangement is the case of two subsystems side by side coupled by a moving piston, which allows the analysis of the celebrated “adiabatic piston” problem.<sup>6,22,23,26–28</sup> A third geometry is the same as the previous one, but with the two subsystems on the vertical. Finally, the last setup involves two-subsystems side by side and with a piston on the top of each of them, in order to study the constant pressure calorimeter.<sup>15,16</sup>

### A. Heat and the first law

The first geometry we want to investigate corresponds to a subsystem  $A$  similar to the base model, namely a classical ideal gas in a container with a moving piston. However, subsystem  $A$  is in now contact with another subsystem  $B$ , of fixed volume, as represented in Figure 5. The *complete* system (formed by gases  $A$  and  $B$  and the piston) is isolated, but subsystems  $A$  and  $B$  can exchange energy with the piston and therefore the system  $(A + B)$  is not isolated. Furthermore, subsystems  $A$  and  $B$  can also change energy through the common border. The conclusions from our base model apply to the new system  $(A + B)$ .

As the complete system is surrounded by vacuum, we have

$$U = U_A + U_B , \quad (31)$$

where  $U$  is the total internal energy, and  $U_A$  and  $U_B$  are the internal energies of subsystems  $A$  and  $B$ , respectively.

We can now write [*cf.* Equations (24)–(25)]

$$W = - \int \tilde{P} dV = \Delta U = \Delta U_A + \Delta U_B . \quad (32)$$

As before, between two points where the piston is at rest the work of the dynamic force is equal to the work of the weight. The last expression can be written as

$$\Delta U_A = W - \Delta U_B , \quad (33)$$

or, defining

$$Q = -\Delta U_B , \quad (34)$$

$$\Delta U_A = W + Q . \quad (35)$$

Evidently, this is the usual formulation of the first law of thermodynamics (the symbol  $W$  is often defined with the symmetric sign, *i.e.*, as the work done by the system, so that  $\Delta U_A = Q - W$ ). The quantity  $Q$  is denoted by *heat* or heat exchanged with subsystem  $B$ . Its symmetric simply corresponds to the *variation of the internal energy of subsystem B* or, similarly, the energy transferred from  $A$  to  $B$ . The first law is thus a particular form of writing the principle of conservation of energy.

It is important to emphasize that the introduction of heat in this simple but clear way gives a valuable contribution to help avoiding some of the most common traps related to this concept, as further discussed in Section IV C.

## B. Temperature and the heat reservoir

One interesting result that can be easily obtained is the equality of temperatures of subsystems  $A$  and  $B$  described in Section IV A along reversible transformations. In fact, from (31)

$$dU = dU_A + dU_B . \quad (36)$$

Here, noting that  $V_B = \text{const.}$  and that for a reversible transformation  $dS = 0$  ,

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS - P dV = -P_A dV_A . \quad (37)$$

On the other hand,

$$dU_A = T_A dS_A - P_A dV_A , \quad (38)$$

and

$$dU_B = T_B dS_B , \quad (39)$$

where  $T_A$  and  $T_B$  are defined by Equation (21). Combining these expressions, we obtain

$$T_A dS_A + T_B dS_B = 0 . \quad (40)$$

Finally, assuming the entropy to be an extensive quantity (an assumption that can be motivated and discussed) and since the transformation is reversible,

$$dS = dS_A + dS_B = 0 , \quad (41)$$

from where, using (40),

$$T_A = T_B , \quad (42)$$

which is the result we wanted to achieve. It shows that temperature is a property characterizing the state of equilibrium of the two subsystems.

The limiting case in which the subsystem  $B$  is infinite is important, as it coincides with the idea of a small subsystem in contact with a *heat reservoir*. In this case, subsystem  $B$  is so big that an energy exchange with the smaller subsystem does not change its temperature. This intuitive notion can be verified as follows. If the energy density is uniform, in each unit volume  $i$  of the heat reservoir we have the same volume  $V_i$  and the same internal energy  $U_i$ . Hence, since  $U_i = U_i(S_i, V_i)$ , all unit volumes have as well the same  $S_i$ . As the system is infinite, any finite transfer of energy will not change its energy per unit volume. Therefore,  $V_i$ ,  $U_i$  and  $S_i$  are not modified by a finite energy transfer to or from the heat reservoir. All quantities being the same, the derivatives (21) are also the same and the temperature of the heat reservoir always remains unchanged. Equation (42) tells us that in this case a reversible transformation is an isothermal transformation at  $T = T_B$ . Moreover, since  $dS_A = -dS_B$ , using (39) and (34),

$$dS_A = \frac{dQ}{T} . \quad (43)$$

### C. The adiabatic piston

The so called “adiabatic piston” problem corresponds to a system involving two ideal gases contained in a horizontal cylinder and separated by an *insulating piston that moves without friction*, as shown in Figure 6. This system is more complex than the previous ones and was treated by many authors, using different approaches and techniques.<sup>6,22,23,26–30</sup> Worth noting are the qualitative kinetic description by Feynman,<sup>6</sup> the molecular dynamics calculations by Mansour and co-workers<sup>26,28</sup> and the classical thermodynamics analysis by Gislason.<sup>22</sup>

Classical thermodynamics analyses are of major interest here. As pointed out in our previous work,<sup>23</sup> a careful use of thermodynamics must give the same final result as molecular dynamics, because the latter is a microscopic interpretation of the former. However, too commonly this is not the case, a fact that strikingly exemplifies the difficulties associated with the formalism of thermodynamics. Gislason makes a very interesting and enlightening



discussion of the problem,<sup>22</sup> focusing on the shorter time-scale, when the two gases evolve to a situation of equal pressures. Though, he does not address the second phase, when the gases evolve to a situation of equal temperatures, discussed qualitatively by Feynman<sup>6</sup> and formally derived in our previous work.<sup>23</sup> On the other hand, Anacleto and Anacleto,<sup>29</sup> just to give one example, make a faulty investigation of the problem, claiming that the piston does not reach a final state of equilibrium, instead keeping oscillating indefinitely. Furthermore, they allege that entropy remains constant, due to the absence of friction, which is not the case.

The main difficulty with this problem lays in a negligent use of language. As a matter of fact, the word “adiabatic” is too swiftly associated with “no heat exchange.” Moreover, “heat exchange” is rarely defined with generality, but we immediately are lead to impose the mathematical condition  $dQ = 0$  in the calculations.

The correct solution within the framework of thermodynamics was presented previously,<sup>23,27</sup> and the reader should refer to those papers for the details on the formal use of the thermodynamic laws. Quoting from our former work,<sup>23</sup> by an “adiabatic piston” it is meant a piston *with zero heat conductivity*. If the piston is held in place (for instance, if it is fixed to the box by screws), then there is no “heat transfer” from one subsystem to the other. Even though, if the piston is released, both systems exchange energy via collisions with the piston, as they are coupled through the conditions of constant total volume and total energy, where the kinetic energy of the piston has to be taken into account. The evolution to a stage of mechanical equilibrium of equal pressures *has nothing to do with friction*: it is simply a result of the dissipative character of the dynamic pressure, discussed in our base model. There is indeed an entropy increase, as also acknowledged by Gislason in his analysis of the first phase of the problem.<sup>22</sup> Gislason in fact provides significant physical insight by identifying the damping of the piston motion as a result of the dynamic pressure on it, “because the pressure is greater when the piston is moving towards the gas than when the piston is moving away from the gas.”<sup>22</sup>

After the equalization of pressures the coupling between both subsystems remains, only the kinetic energy of the piston becomes negligible. Still, the collisions between the gas particles and the piston will make the piston jiggle, *allowing an exchange of energy* between both gases.<sup>6,23</sup> These energy exchanges will always take place, despite the piston being non thermal conductor and the absence friction, as they are simply a result of the momentum transfer

in the collisions (*cf.* the discussion by Feynman<sup>6</sup>). And, as pointed out in Section IV A, these energy exchanges can be formally treated as heat exchanges. Therefore, in this second phase the system evolves to a situation of equal temperatures, with  $\Delta U_A + \Delta U_B = 0$ . In this case, if we write the first law for gas  $A$  we have  $Q = -\Delta U_B \neq 0$  [Equation (39)], and *the condition  $dQ = 0$  cannot be imposed.*<sup>23</sup> In fact, we have instead  $dQ_A = -dQ_B$  [equation (16) in Ref.<sup>23</sup>]. Notice that the different quantities somewhat lose their energetic interpretation, merely being a result of the mathematical formalism.

From the discussion above, it is clear that during both phases of evolution there *has to be* an “heat exchange,” according to the formalism of thermodynamics, no matter whether the piston was defined as “adiabatic,” which might seem a bit shocking at first. The problematic use of language is easily avoided if we leave behind a formulation of the first law which to some extent still dates from the time of caloric, and instead keep in mind its introduction as suggested in Section IV A and from Equation (34). Then there is no doubt that the “adiabatic piston” system allows the energy exchange between both subsystems. And it is by no means shocking to assert that the internal energy of each subsystem changes due to the collisions, even for a piston with zero heat conductivity and moving without friction.

#### D. Further generalizations

From a general introduction of the first and second laws of thermodynamics and an early alert on the dangers of a blind use of the mathematical formalism, as outlined in the previous sections, it is possible to proceed to more complicated and richer systems. This paper would become too lengthy if we would discuss them in detail here. Nevertheless, due to their importance we find justified to delineate few of them already.

##### 1. The adiabatic piston in a gravitational field

A natural generalization is to consider the adiabatic piston from the previous section, but now in a vertical configuration and under the effect of gravity. In this case the work done by the dynamic force has two terms, one for each gas. This case follows very closely the adiabatic piston discussed in our previous work.<sup>23</sup>

The conservation of energy reads

$$dU_A + dU_B + dE_{pot} + dE_k = 0 , \quad (44)$$

where  $dU_A$  and  $dU_B$  are the internal energies of subsystems  $A$  (bottom) and  $B$  (top), respectively, whereas  $dE_{pot}$  and  $dE_k$  are the piston gravitational potential energy and its kinetic energy, respectively. If the piston has mass  $M$  and area  $S$ , and noting that  $dE_{pot} = (Mg/A)dV_A$ , the reader is invited to adapt our former calculations<sup>23</sup> and verify that the equilibrium condition corresponds to equality of forces on the piston *and* equality of temperatures,  $P_A = P_B + Mg/A$  and  $T_A = T_B$ .

Furthermore, since  $dV_A + dV_B = 0$ , the work of the resultant of the forces on the piston is [cf. (14)]

$$(\tilde{P}_A - \tilde{P}_B)dV_A - \frac{Mg}{A}dV_A = dE_k , \quad (45)$$

Therefore, from (44) and (45) we have

$$(\tilde{P}_A - \tilde{P}_B)dV_A = dE_k + dE_{pot} = -dU_A - dU_B . \quad (46)$$

Finally,

$$\sum_i dU_i = \sum_i \left( -\tilde{P}_i dV_i \right) = \sum_i (-P_i dV_i + T_i dS_i) \neq \sum_i (-P_i dV_i) \quad (47)$$

with  $i = \{A, B\}$  and

$$\sum_i T_i dS_i = - \sum_i (\tilde{P}_i - P_i) dV_i . \quad (48)$$

Exactly like the case of the “adiabatic piston,” the direct use of the first law for one of the gases and the assignment of physical meaning to the quantity  $Q$  is not straightforward, as neither the conditions  $dQ = 0$  and  $dU_i = -P_i dV_i$  nor even  $dU_i = -\tilde{P}_i dV_i$  can be imposed.<sup>23,31</sup>

## 2. The constant pressure calorimeter

One important configuration in practical applications is the constant pressure calorimeter.<sup>15,16</sup> The system can be idealized by adding a piston to subsystem  $B$  from Figure 5 to keep it at constant pressure. The new configuration is depicted in Figure 7.

Let us denote the pressure exerted by the piston on subsystem  $B$  by  $P_0$ . In other words,  $P_0 = M_B g / A_B$ , where  $M_B$  is the mass of the piston on subsystem  $B$  and  $A_B$  its area. Likewise, let us define  $P_e = M_A g / A_A$ .

Consider first a reversible transformation. In this case, the pressure  $P_B$  is always equilibrated at  $P_0$  and there is no difference between  $P_B$  and  $\tilde{P}_B$ . Therefore, defining the enthalpy  $H$  as

$$H = U + PV \quad (49)$$

and the specific heat at constant pressure  $C_P$  from

$$(dH)_P = C_P dT , \quad (50)$$

we have

$$dH_B = d(U_B + P_B V_B) = dU_B + P_B dV_B = T_B dS_B \equiv C_{P,B} dT_B . \quad (51)$$

To address the general case of an irreversible transformation (for instance if we would initially have  $P_e > P_A$ ), we note that the conservation of energy reads

$$dU_A + dU_B + dE_{pot,A} + dE_{k,A} + dE_{pot,B} + dE_{k,B} = 0 , \quad (52)$$

where  $dE_{pot,A}$  and  $dE_{k,A}$  are the potential and kinetic energies of piston  $A$ , given by Equations (14) and (15), respectively, and the same for piston  $B$ . Hence, we still have

$$dU_A + dU_B = -\tilde{P}_A dV_A - \tilde{P}_B dV_B . \quad (53)$$

Between two points where both pistons are at rest ( $\Delta E_{k,A} = \Delta E_{k,B} = 0$ ) we have, successively,

$$\Delta U_A + \Delta U_B = -P_e \Delta V_A - P_0 \Delta V_B , \quad (54)$$

$$\Delta U_A = -P_e \Delta V_A - (P_0 \Delta V_B + \Delta U_B) = -P_e \Delta V_A - \Delta H_B , \quad (55)$$

where  $\Delta H_B = \int C_{P,B} dT$ . If the specific heat at constant pressure  $C_{P,B}$  is constant, we can finally write

$$\Delta U_A = -P_e \Delta V_A - C_{P,B} \Delta T_B . \quad (56)$$

Thus, if we want to apply the first law of thermodynamics (35) to gas  $A$ , the second term on the r.h.s. corresponds to an energy exchange with subsystem  $B$  that we can identify with the heat exchanged with subsystem  $B$  between two points of equilibrium.

## V. DISCUSSION

We have presented a simple and clear model to introduce thermodynamics, which reveals and naturally solves some of the difficulties underlying the concepts of work and heat in the formulation of the laws of thermodynamics.

The first step is the extension of the notions of kinetic and potential gravitational energies to the one of *internal energy*, inferred in Section II from the analysis of extended deformable bodies. Subsequently, the base model presented in Section III shows that if we assume that part of the universe has potential and kinetic energy which depend only on the position and velocity, as in the study of *mechanics*, then the remaining part of the universe – in this case the gas – has an energy which depends on the position and entropy,  $U = (S, V)$ , the subject of *thermodynamics*.

It is pointed out that the *dynamic force* on the piston has a *dissipative character*, even if we have only conservative forces and there is no friction. The second law of thermodynamics is then readily obtained (sections III A and III B). An interesting idealized situation of our base model corresponds to a very simple one-dimensional picture, namely, a gas formed of  $N$  punctual particles of mass  $m$  moving only on the vertical direction under the action of gravity, and colliding elastically with the piston of mass  $M$ . There is no friction and the particles do not interact directly with each other. Even this straightforward model is enough to understand the dissipative character of the dynamic force, the approach to equilibrium and, thus, irreversibility. In the thought case where all particles are initially exactly at the same height and have exactly the same velocity, the situation is the same as with a one-dimensional elastic collision between two point masses (one of mass  $Nm$  and the other of mass  $M$ ). Therefore, the piston remains oscillating indefinitely. The dissipative character of the dynamic force does not appear and the entropy remains constant. The system “has no imagination,” the accessible volume in phase-space remaining very limited. However, if the masses  $m$  are not exactly “on phase,” if there is a small difference in their positions or speeds, the dissipative character emerges and there is an entropy increase.<sup>37</sup> The accessible volume in phase-space has now increased. The key factor leading the evolution to equilibrium is the *interaction* between the different particles, even if it is kept to a minimum and only takes place indirectly through the collisions they experience with the piston. These ideas are in line with the pioneering works by Ludwig Boltzmann. A somewhat poetic statement

expressing this main result would be “thermodynamics is mechanics with imagination.”

We believe that computer simulations are a powerful tool to explore the qualitative behavior of a model, as underlined by Gould and Tobochnik.<sup>32,33</sup> A systematic exploration of simulations of the simplified one-dimensional model just described, including the analysis of the accessible phase-space and equipartition of energy, will be performed in a future publication. A very interesting simulation of a similar system, where collisions between particles and motion in two dimensions are considered – but not the gravitational force on the particles – is available online from the NetLogo Models Library.<sup>34,35</sup> In this case, as the interactions between particles are easier to occur, the evolution to equilibrium is much faster than in our simplified one-dimensional case and the effect is easily obtained.

The approach to equilibrium raises the question of *irreversibility*. Still using the base model, irreversibility and the increase in entropy are seen to be a result of the dissipative character of the dynamic force discussed above. The example of the compression/expansion with sand grains illustrates that the higher the unbalance between the dynamic and static pressures, the higher the increase in entropy, as also shown by Gislason.<sup>22</sup> The importance of the so-called “quasi-static” formulations is then easily understood. It is the work of the dynamic force that is equal to the variation of the internal energy of the gas [Equation (18)]. In a quasi-static process the work of the dynamic force is a good approximation for the work of the static force during part of the trajectory of the piston, the variation of entropy being nearly zero [Equation (23)]. For any real process it is not possible to actually return to the initial conditions and it is thus necessary to generalize the idea of potential energy from mechanics, which is a function only of the variable of configuration (or deformation),  $V$ , to the gas internal energy, function of one additional variable,  $S$ . It is noted that mechanics corresponds to isentropic thermodynamics, *i.e.*, to the situations where  $U = U(V)$  (and so the internal energy is a potential energy), either by the nature of the problem or as an approximation.

The traditional development of thermodynamics defines the internal energy first as a function of  $V$  and  $T$ . Noting that  $(\partial U/\partial T)_V = C_V > 0$  we could then be induced to think that mechanics would correspond to isothermal thermodynamics. However, this is not the case. During the sand-grain transformation of the base model, where  $P \simeq \tilde{P}$ , we have  $dT \neq 0$ . In particular, during the compression and the expansion we have, respectively,  $dT > 0$  and  $dT < 0$ . The transformation is thus characterized by  $dS = 0$  and not by

$dT = 0$ . That being so, mechanics indeed corresponds to isentropic thermodynamics and not to isothermal thermodynamics, reinforcing the importance of considering  $S$  the conjugate variable for  $V$ .

The idea that when a system returns to the initial position, such as after the compression-expansion from our base model, it has an higher internal energy than at the beginning [Equation (9)], is fairly counterintuitive. This comes from the fact that physical systems are often surrounded by a thermostat, which prevents the manifestation of the thermodynamic phenomenon. A good example is the deformation of an elastic material or a spring, such as the case of a spring hanging on the vertical holding a certain mass. The situation is very much alike to our base model and a similar analysis as in Section III A can be made. New masses can be added and removed to the spring and new equilibrium positions can be found. In this case, the excess energy is exchanged with the surroundings and apparently we return to the initial state. The entropy variation is in the surrounding environment and we are conducted to think that everything happens as if the dynamic force could be approximated by the static force and internal dissipation would not exist, as the spring returns to the initial length and the force to its initial value. However, we know that the energy increase of the environment is equal to the work of the dynamic force, which is equal to the changes of gravitational potential energy of the masses that are now at a lower level.

The heat reservoir was analyzed in Section IV B, as a limiting case of the case of energy exchanges between two subsystems, which can be described as *heat* exchanges. The first law is also derived in this context (Section IV A). Furthermore, the notion that “there is no such thing as perpetual motion with weight lifting machines”<sup>6,7</sup> (Section II) can now be easily extended to account for the second law. In fact, this statement reflects the conservation of energy when entropy is not involved, so that  $U = U(V)$ . In this case,  $W = \Delta U$  and, when the system returns to its initial position,  $\Delta U = 0$  and hence  $W = 0$ . For a general case, with friction or even simply the reorganization of the internal energy as a result of the action of the dynamic force,  $U = U(S, V)$ , with  $\Delta S > 0$ . When the system returns to its initial position we have  $\Delta U > 0$ , so that  $W > 0$ , leading to the conclusion that “there is no perpetual motion at all.”<sup>6</sup> This inference is valid both when subsystem  $B$  is finite (*cf.* Figure 5) and in the limiting case of an heat reservoir, in what may be seen as a generalization of the Kelvin-Planck formulation of the second law.

The analysis of the adiabatic piston problem – Section IV C – has to be done with care.

It is no longer possible to separate the energy-momentum exchanges of the particles from the two subsystems with the piston into quantities “work” and “heat” with clear energetic meaning. The correct and complete solution of this problem may contribute to illustrate the difficulty in assigning a physical meaning to these two quantities, as they appear in the laws of thermodynamics.<sup>23,27</sup> The “jiggling piston” further provides a perfect bridge between thermodynamics and the microscopic structure of matter, Feynman’s *atomic hypothesis* mentioned in the introduction to this paper,<sup>6</sup> and the importance of the keeping it in mind. Although the final result of equal pressures and temperatures can be obtained without referring to heat and thermodynamics,<sup>6</sup> the complete analysis allows a further exploration of the microscopic interpretation of entropy.<sup>36</sup> As a matter of fact, it is worth stressing that after the equalization of pressures there are configurations in the vicinity of this mechanical equilibrium with greater global entropy, and the system will move towards these configurations. As a consequence, the system will indeed access the different available microscopic configurations and move as a result of a blind entropic process, in accordance with Boltzmann’s basic ideas and his microscopic interpretation of entropy. The latter also furnishes an explanation on the additive property of entropy.

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- <sup>37</sup> It can be noted that the notion of “exactly the same height and exactly the same velocity” does not make sense in quantum mechanics. However, it is not necessary to invoke quantum mechanics for the point we are making here.

## Figures

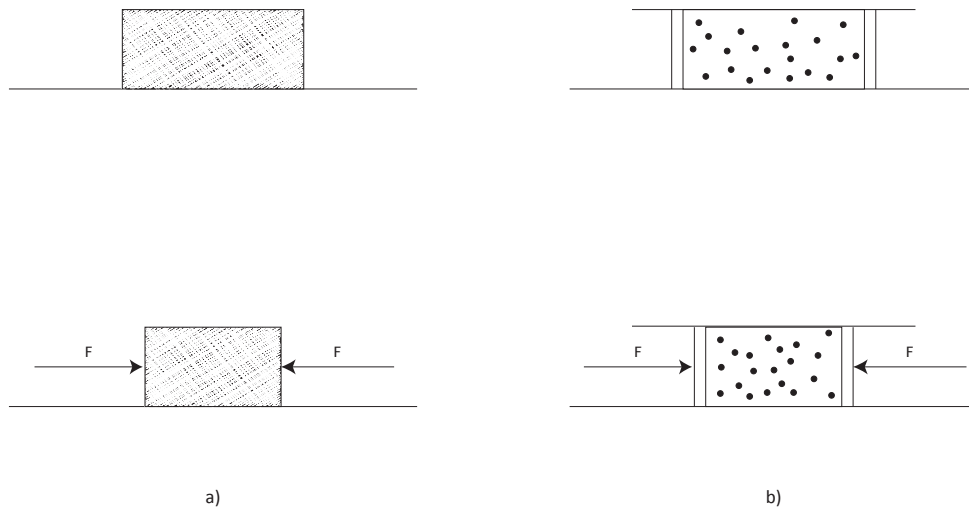


FIG. 1: A body deforms under the action of two forces of equal magnitude: a) macroscopic picture; b) microscopic picture, the body being an ideal gas in a container with movable walls.

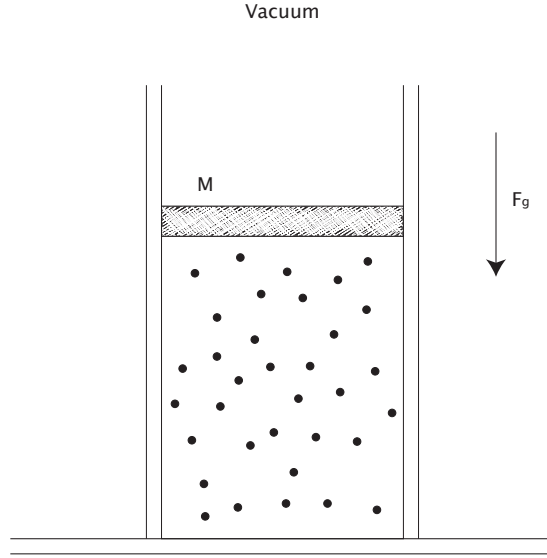


FIG. 2: The base model: an ideal gas is contained in a cylinder with a frictionless movable piston of mass  $M$  on the top.

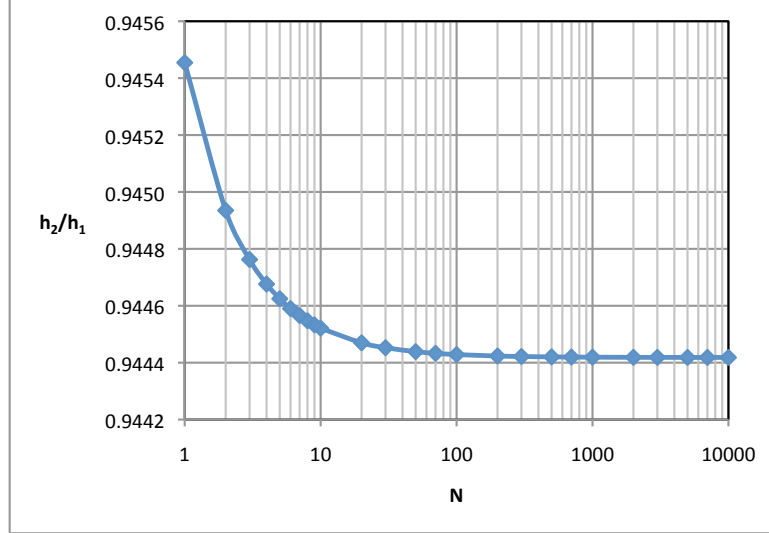


FIG. 3: Final equilibrium height of the piston after the compression, as a function of the number  $N$  of masses used to increase the total mass from  $M_0 = 10$  kg to  $M = 11$  kg (see text).

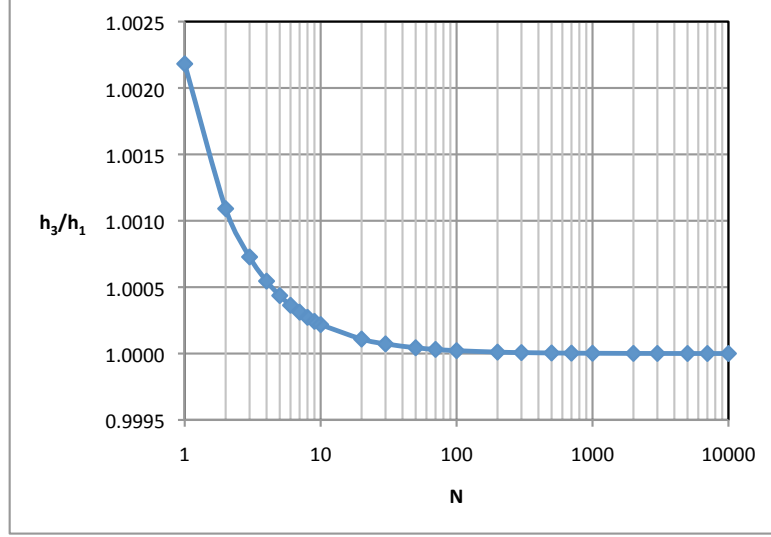


FIG. 4: Final equilibrium height of the piston after compression and expansion, as a function of the number  $N$  of masses used both to increase the total mass from  $M_0 = 10$  kg to  $M = 11$  kg and then to decrease it back to  $M_0$  (see text).

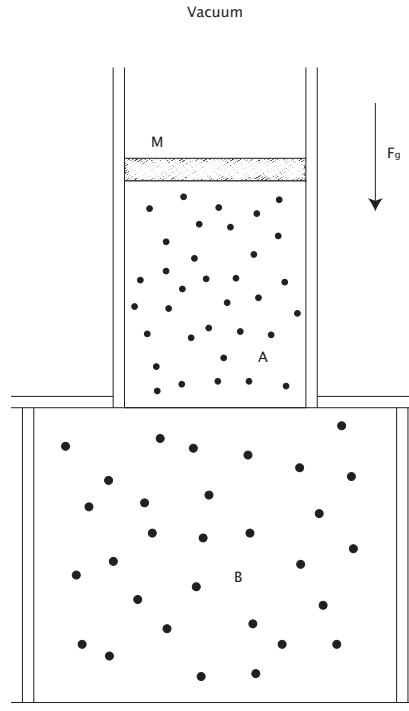


FIG. 5: Two subsystems,  $A$  and  $B$ , which can exchange energy through a common border. A frictionless piston of mass  $M$  can move and modify the volume of subsystem  $A$ .

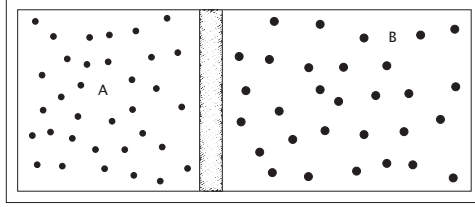


FIG. 6: Two subsystems,  $A$  and  $B$ , which *can* exchange energy through a moving “adiabatic” and frictionless piston.

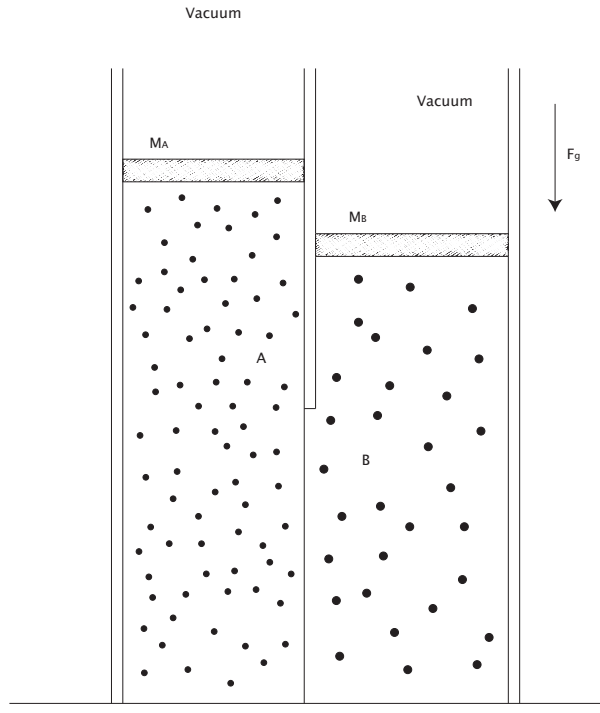


FIG. 7: The constant pressure calorimeter can be schematically represented by two subsystems,  $A$  (gas) and  $B$  (calorimeter), which can exchange energy through a common border. A frictionless piston of mass  $M_B$  keeps subsystem  $B$  at constant external pressure (instead of constant volume, as in Figure 5).